CATALYTIC COMBUSTION SURFACES
AND METHOD FOR CREATING
CATALYTIC COMBUSTION SURFACES

This application is a continuation of United States Patent Application Serial No.

09/920,132, filed August 1, 2001 and entitled "CATALYTIC COMBUSTION SURFACES AND

METHOD FOR CREATING CATALYTIC COMBUSTION SURFACES, the entire disclosure of which

is hereby incorporated by reference herein as if being set forth in its entirtey.

The present invention relates generally to increasing the efficiency and reducing

emissions of internal combustion in engines. More particularly, the present invention relates

generally to the application of coatings to internal combustion engines for the purpose of

reducing unwanted emissions, and more particularly to the application of nickel coated

5   materials to the combustion surfaces of reciprocating piston internal combustion engines to

promote fuel combustion efficiency.

Background

Internal combustion engines using hydrocarbon fuels are widely used due to their

ability to create mechanical energy from a fuel that provides power for a sufficient time

10   period without requiring complex or large fuel storage associated with the engine. Internal

combustion engines may utilize the Diesel cycle, wherein self-ignition of the hydrocarbon fuel is used to initiate combustion of the hydrocarbon fuel. Hydrocarbon fuel used in Diesel cycle engines typically contains heavier petroleum fractions than the hydrocarbon fuel used in engines having spark ignition systems. The fuel having the heavier hydrocarbon fractions

5   is typically called diesel fuel, even though the fuel can be used in spark ignited and spark assisted ignition engines designed to combust the heavier fractions. Engines using diesel fuel are widely used in commercial vehicles due to inherent efficiencies associated with the diesel fuel and the diesel cycle. Fuels utilizing the heavier hydrocarbon fractions tend to be less expensive than fuels using lighter hydrocarbon fractions, due to lower demand and

10   reduced refining costs. The use of the higher fractionated fuel allows diesel fueled engines to utilize a higher compression ratio, resulting in a higher combustion efficiency.

Although diesel fueled engines are preferred in commercial applications, the use of diesel fueled engines is not without room for improvement. Normal operation of diesel fueled engines results in the production of harmful emissions, including soot and unburned

15   hydrocarbon molecules. Diesel fueled engines tend to have higher exhaust emissions, particularly soot, when heavily loaded, or run in an improper state of tuning. Also, the cost of operating a diesel fueled engine is heavily influenced by the cost of the fuel being used in the engine.

The use of catalytic materials in the exhaust stream of hydrocarbon fueled engines

20   has been implemented to reduce unwanted emissions. The catalytic effect in the exhaust stream accomplishes a reduction of unwanted emissions, but accomplishes the reduction of the unburned hydrocarbons downstream from the combustion chamber, such that energy released through the catalytic reaction is not utilized, and must be rejected as waste heat.

Thus, the catalytic reaction provides no efficiency in the conversion of the hydrocarbon fuel into mechanical energy.

Technologies such as low heat rejection (LHR) coatings are being developed to improve the efficiency of fuel combustion in diesel fueled engines. LHR engines rely on the

5   use of combustion surface coatings which form insulation or thermal barriers, thus retaining the heat of combustion within the combustion volume, allowing more of the combustion energy to be converted into mechanical energy, thus reducing the fuel consumption for a given power level. LHR technologies are presently directed towards the use of ceramic coatings applied to the combustion surfaces of an engine to inhibit heat transfer from the

10   combustion products to the engine block and heads. The use of ceramic materials, however, raises issues related to lubrication of the reciprocating components, as well as to the formation of deposits on the coating surfaces (referred to as "coking") which inhibit combustion efficiency.

U.S. Patent No. 5,987,882 to Voss et al. is directed towards combining a ceramic

15   layer with an oxidation catalyst material, such as a rare-earth metal oxide. The described multi-component coating is claimed to increase the efficiency of combustion by retaining heat within the volume where the coating is applied. A benefit associated with such retention is an improved performance of the catalyst material, due to increased chemical action of the catalyst at elevated temperatures. Application of the coating to combustion

20   surfaces of a reciprocating engine is described in the patent. The application described requires the integration of a bond coat as a bonding substrate below the insulative coating. The bond coat used for the described examples consisted of a 4 mil metal-aluminum-chromium-yttrium alloy, preferably using nickel, cobalt, or iron for the metallic component.

The use of rare-earth metallic oxide catalytic materials is, may be, however, susceptible to poisoning of the catalyst material. Sulfur contained in fuel to which the catalyst material is exposed prevents catalysts from functioning properly by causing sulfate production that inhibits catalyst regeneration. Accordingly, the use of catalytic technologies

5   which incorporate materials such as platinum and praeseodymium oxide may be problematic when used with current diesel fuel, which contain sulfur levels sufficient to cause poisoning of the catalyst materials.

Other efforts towards improving the combustion efficiency of diesel fueled engines have been directed towards improved fuel formulations, combustion chamber size and

10   shape, and the use of pre-ignition chambers. Each of these technologies may provide some gain with respect to combustion efficiency, however the costs associated with their implementation are not optimal when considered in light of the commercial applications in which the diesel fueled engines are used. The expense of reformulated fuels directly increases the operating costs of engine utilization. Intricate combustion chamber shapes, pre-

15   ignition chambers, and ceramic-metallic coatings add to the production cost and complexity of the engines, as well as complicate maintenance issues and potentially the reliability of the engines themselves.

The use of coatings on engine components, including diesel fueled engine components, has generally been directed towards reduction of friction between components

20   of the engine. The principal areas of interest have been the walls of the cylinder bore and the sealing rings, which extend between the skirt of a piston and the cylinder bore. U.S. Pat. No. 5,866,518 to Dellacorte et al. describes a composite material for use in high temperature applications. The Dellacorte composite consists primarily of chromium dioxide (60-80% by

weight) in a metal binder having at least 50% nickel, chromium, or a combination of nickel and chromium. The greatest proportion of binder described is 60%, such that the highest proportion of nickel used in the coating is 30%, at which point no chromium is included. The Dellacorte patent describes the composite as providing a self-lubricating, friction and

5   wear reducing material to be applied to the sealing rings.

U.S. Pat. No. 5,292,382 to Longo describes a sprayable molybdenum/iron coating which may be sprayed on piston rings as a means of reducing friction. The composition of the Longo material is described as 25-40% molybdenum, 4-8% chromium, 12-18% nickel, and 25-50% iron, with carbon, boron, and silicon additionally included in the composition.

10

Summary of the Invention

The present invention is directed towards a combustion chamber surface coating and method for applying the coating to improve the combustion efficiency of internal combustion engines, particularly, but not necessarily limited to, those utilizing diesel fuel.

15   The coating improves the combustion efficiency through a catalytic reaction with the hydrocarbon based fuel which causes hydrocarbon molecules to disassociate into free radicals at an accelerated rate. The higher concentration of free radicals drives the combustion reaction to a faster and more complete combustion of the hydrocarbon fuel, thus obtaining energy from the fuel more efficiently, as the more complete combustion provides

20   more power per unit of fuel and less unwanted emissions.

The catalytic reaction is accomplished by providing a nickel surface on components which form the combustion chamber of the engine. The nickel reacts with the hydrocarbon

molecules in a catalytic reaction which produces the free radicals. Although the nickel is believed to be the component driving the reaction, the use of a pure nickel surface may be limited only by the inactive characteristics of nickel in providing a surface with sufficient structural characteristics to provide a durable and reliable surface. Accordingly, the nickel

5   may be alloyed with other materials to provide sufficient durability and reliability when used in the combustion chamber environment. Presently, an alloy comprising nickel, chromium, and iron has been employed, however other materials may be substituted, interchanged, or included in the composition as indicated by desired other properties.

The amount of free radicals which can be dissociated from hydrocarbon molecules is

10   generally understood to be dependant on the contact of the hydrocarbon molecules and the nickel, and thus the amount of exposed surface area of the nickel appears to be related to the improvements in combustion efficiency gained. In addition to increasing the coating area, the surface of a coated area may be increased by forming the coating with a less smooth surface. Accordingly, the nickel surface may be formed by applying a coating according to

15   the present invention to surfaces which form the combustion chamber by a high velocity oxygen flame process. This deposition method typically results in a coating having sufficient bonding strength to underlying structure to provide sufficient durability, while providing a surface roughness which limits coking of the engine while providing increased contact area between the nickel and hydrocarbon molecules.

20   In a first form, the present invention may be embodied in an internal combustion engine having at least one reciprocating component, a bore within which the at least one reciprocating component reciprocates, and a closure over one end of the bore. The reciprocating component has a combustion face. The reciprocating component reciprocates

relative to the closure between TDC and BDC positions. A combustion volume is defined at least in part by the combustion face of the reciprocating component, and a surface of the closure. At least a portion of the surfaces which define the combustion volume are coated with a metallic coating which includes nickel, such that when the combustion face is at the

5   position at which the combustion face is at a closest point to the closure, it has been noted that it is preferable to have at least 10% of the surfaces which define the combustion volume are coated with the coating, although lesser amounts of coating may also have efficiency.

In an alternate form, the present invention may be embodied in an internal combustion engine having a combustion volume and a reciprocating piston, with the

10   reciprocating piston having a combustion face and the combustion engine further having a combustion volume. The combustion volume may be bounded by combustion surfaces. The combustion surfaces may include the combustion face of the reciprocating piston. A portion of the combustion surfaces equivalent in area to one tenth or more of the combustion face area is coated with a composition that is exposed to combustion gases. In its form, the

15   composition may include between approximately 2% and approximately 80% nickel, between approximately 10% and approximately 30% chromium, and between approximately 10% and 90% iron, although other compositions may be possible.

In a further form, the present invention may be embodied in a process for reducing particulate emissions in a diesel fuel powered internal combustion engine, wherein the

20   internal combustion engine comprises at least one cylinder having a combustion chamber. The process includes the steps of coating at least a portion of the inner surfaces of the combustion chamber with a composition which may include between 2% and 80% nickel

and 10% and 40% chromium, (although other compositions may be possible) where the coating forms a surface exposed to combustion gases.

Brief Description of the Drawings

5   Figure 1A is an illustration of an internal combustion engine to which the coating of the present invention has been applied, illustrating the combustion surfaces associated with the coating of the present invention.

Figure 1B is an illustration of an internal combustion engine to which the coating of the present invention has been applied, illustrating the piston in the top-dead-center

10   (hereafter "TDC") position.

Figure 1C is an illustration of an internal combustion engine to which the coating of the present invention has been applied, illustrating the piston in the bottom-dead-center (hereafter "BDC") position.

Figure 2 is an illustration of the head of a Yanmar TS180C research engine used in

15   the first illustrative embodiment, to which the coating of the present invention has been applied, identifying characteristics associated with the engine.

Detailed Description of the Invention

Referring now to Figure 1, wherein like reference numerals indicate like elements, there is shown the components of a diesel engine 100 to which the coatings of the present invention have been applied.

5   As shown in Figure 1, a simple Diesel cycle reciprocating piston internal combustion engine includes a piston 102 that reciprocates in a bore 104. The bore 104 is closed at one end. The reciprocating piston 102 reciprocates between two positions. One position, commonly referred to as top dead center (shown in Figure 1B and hereafter referred to as "TDC" 106), occurs when the piston is at its closest point of travel to the closed end of the

10   bore. The other position, commonly referred to as bottom dead center (shown in Figure 1C and hereafter referred to as "BDC" 108), occurs when the piston 102 is at its farthest point of travel from the closed end of the bore 104. Typically, the walls of the bore 104 may be integrally formed in an aluminum or cast iron engine block 110, or may be formed by liners inserted into an engine block 110. The walls of the bore 104, in conjunction with the closure

15   at the one end of the bore 104 and the combustion face 112 of the piston 102, form the boundary of the combustion volume 114 associated with the piston 102. Owing to the motion of the reciprocating piston 102, the volume of the combustion volume 114 is not fixed, but rather varies with the position of the piston 102 within the bore 104.

In a typical engine, such as a diesel engine 100 to which the present invention may

20   be applied, the closed end of the bore is formed by a head 116 that is bolted over one end of the bore 104. The head 116 is typically formed from cast iron. The head 116 typically includes a pocket 118 formed into the head 116 to provide a shaped pocket to improve the flow of an air/fuel mixture into and out of the combustion volume 114, which is typically

accomplished through intake 120 and exhaust valves 122. The pocket 118 in the head 116 is typically called the combustion chamber, although the pocket 118 does not provide all of the surfaces that define the volume 114 within which combustion occurs. The intake 120 and exhaust 122 valves are typically located in the head 116 for manufacturing and maintenance

5   concerns. When the valves 120, 122, are located in the head 116, the face of the intake valve 124 and the face of the exhaust valve 126 may form portions of the surfaces that form the combustion volume 114.

Accordingly, the surfaces to which the air/fuel mixture is exposed while the engine 100 is operating, thus bounding the combustion volume, may include, but are not limited to,

10   the portion of the head and valves which close the bore 104, the side walls of the bore dependant on the position of the piston 102, and the combustion face 112 of the piston. Additionally, the use of sealing rings 128 between the piston 102 and the bore 104 may result in a surface of a sealing ring 128 forming a portion of the surface which bounds the combustion volume 114.

15   Application of the nickel coating of the present invention to these surfaces causes exposure of hydrocarbon molecules to the nickel that forms a portion of the coating. It is believed that the hydrocarbon molecules transform in the presence of the nickel, resulting in a free radical of a hydrocarbon molecule being chemisorbed to the nickel. At temperatures generally above approximately 700 degrees Fahrenheit, the free radical may be dissociated

20   from the nickel coating. Such a free radical may combine more easily with oxygen during the combustion process, resulting in improved combustion efficiency.

Diesel fuels may be categorized by their cetane number. Cetane is $C_{16}H_{34}$ and contains methyl groups that are attached in a manner such that no free radicals are present.

The cetane number is the percentage by volume of cetane in a mixture of liquid methylnaphthalene that gives the same ignition lag as the oil being tested.

When cetane or similar molecules are chemisorbed by metallic nickel, sufficient activation energy is imparted to the cetane molecule (or other hydrocarbon molecules) such that free methyl radicals may be formed. These free radicals may initiate chain reactions in hydrocarbon molecules away from the surface of the metallic nickel. In this manner molecules break up due the catalytic effect to the point where a faster and more complete combustion takes place.

The motion of gaseous molecules comprising the combustion gases is also believed to create friction between the molecules that generates both light and ions to form a corona. The effect of exposed dissimilar metals associated with a partially coated combustion volume is believed to promote the formation of this corona. This corona is believed to be discharged during the intake/combustion cycle, and energy associated with the discharge is believed to further oxidize hydrocarbons, residual carbon monoxide action and nitric oxide.

The corona effect is discussed in US Patent No. 6,047,543 to Caren et al. This patent discusses the use of a 25-watt device for generating a corona that is installed between the engine and a catalytic converter,. It is believed that hydrocarbons, residual carbon monoxide and nitric oxide may be oxidized by ionized oxygen in the presence of free electrons which results from the corona generating device.

The effect of magnetizing a surface to be coated during the coating process, as discussed further below, is believed to further strengthen the corona effect through the formation of additional ions. This magnetic effect is recognized in the waste water treatment

systems, available commercially, where magnets are used to induce ionization and subsequent aqueous oxidation of hydrocarbons to water and carbon dioxide.

Although nickel is the element with which the hydrocarbon molecules react, the coating must have sufficient strength to withstand the pressures and effects of the

5   combustion of the air fuel mixture (not shown). These effects include rapidly cycling temperatures, erosive effects associated with the flow of the air/fuel mixture into the combustion chamber, erosive effects associated with the flow of combusted air/fuel mixture out of the chamber, and corrosive effects associated with the combustion products in the high temperature environment resultant from combustion.

10   Accordingly, the use of a pure nickel coating is not advantageous, in that the nickel does not possess adequate strength to provide the surface unless alloyed with other materials. The addition of chromium and iron has been shown to provide adequate coating properties to provide adequate durability when used in commercial applications. As iron has catalytic properties of its own, the use of iron in the composition both provides needed

15   structural properties, as well as may additionally improve the catalytic effect of the coating. The addition of chromium provides anti-corrosion properties which are beneficial to the durability of the coating. Other metals having catalytic properties, such as, but not limited to, cobalt, rhodium, osmium and iridium may also be incorporated.

The material selected must be chosen with consideration of the ability to withstand

20   the thermal and pressure cycling associated with the combustion conditions within the combustion chamber. It is presently believed that ferritic stainless steels provide advantageous mechanical properties due to their lower tendency to become brittle in response to thermal cycling.

Commercially available alloys may be used for the coating material, such as 17-4 stainless steel or Inconel 625. The use of commercially available alloys may allow reductions in the cost of preparing the coating due to the off-the-shelf nature of the alloy, as opposed to the costs associated with having custom alloys prepared by a supplier. Inconel

5   625 contains a significant amount of molybdenum (approximately about 8-10%) to reduce friction between components in the reciprocating engine. When applied, however, to surfaces such as the combustion face 112 of the piston 102 and the pocket 118 formed in the head 116, the friction reduction properties are unnecessary, since there is no sliding contact between these components and any other component of the engine. Inconel has the further

10   advantage of having a high Nickel content (approximately about >%58) to promote the catalytic interaction between the coating and combustion gases.

Earlier disclosures, such as Longo described above, teach the use of coatings comprising nickel and molybdenum to provide adequate surface characteristics for sealing rings for reciprocating piston internal combustion engines, however the small surfaces of the

15   rings 128 exposed to the combustion chamber are inadequate to provide a significant effect associated with coating larger portions of the combustion surfaces. Additionally, the positioning of the sealing rings 128 typically results in the exposed surface of the top sealing ring 130 being shrouded from the air/fuel mixture by the piston 102.

As the efficiency improvement resultant from the present coating is resultant from

20   interaction between hydrocarbon molecules and the nickel contained in the coating, it may be advantageous to select a surface finish to maximize the surface area of the coating exposed to the hydrocarbon molecules without forming an overly rough surface. Overly

rough surface coatings promote coking of the combustion surfaces, which prevents exposure of the nickel content to the hydrocarbon molecules.

The coating may be applied to combustion surfaces using high velocity oxygen flame spray methods. Other known application methods may also be employed. These methods result in a surface roughness of approximately 200 RMS surface finish, as compared to a surface roughness of approximately 300 RMS associated with normally machined surfaces used in combustion engines. However, any suitable surface roughness may be employed to achieve the desired combustion characteristics.

The selection of surfaces on which to apply the coating may be made based on the cost of applying the coating to the component, the amount of exposed surface area that can be obtained through coating the component, and the utility of the coating on the surface to which the coating is to be applied. Coating friction surfaces such as sealing rings 128 and the bore 104 or bores of the engine may not be beneficial, due to the surface smoothness requirements of these components. The bore walls are not continuously exposed to the combustion products, as the travel of the reciprocating piston 102 alternately exposes and shields the walls from the combustion volume 114. The action of sealing rings 128 sliding across the walls also requires the presence of a lubricant to reduce friction between the components. The presence of the lubricant inhibits the reaction between hydrocarbon fuel molecules and the nickel by being interposed between the nickel surface and the hydrocarbon fuel. Accordingly, coated surface selection must be made in light of the beneficial effect that can be obtained by providing the coating.

The surfaces that provide the greatest benefit from coating are the surface of the pocket 118, the combustion face 112 of the piston 102, and the intake 124 and exhaust 126

-14-

valve faces. If the coating is being applied to a disassembled engine, access constraints are minimal. If only the head 116 of the engine is disassembled, such as during a maintenance action, the coating can be applied to the interior face of the combustion chamber and/or valve faces. Application of a coating to combustion face 112 of the piston may be

5   problematic where the piston 102 remains in the bore 104 of the engine 100, such that an intermediate benefit can be obtained by coating only the interior face of the pocket 118, the faces of the intake 126 and/or exhaust 128, or a combination of these surfaces.

Alternatively, the use of the coating can be extended upstream or downstream from the combustion chamber. Since it is believed that the catalytic effect of the material is a

10   cracking effect as opposed to an oxidation effect, the application of the catalytic material upstream from combustion chamber may allow greater reduction of heavier fractions prior to combustion. This effect will be limited where direct injection is utilized, due to the lack of fuel hydrocarbon, in the intake stream. Additionally, the cracking effect may also reduce unwanted emissions by reducing heavier hydrocarbon fractions in the exhaust stream.

15   First Illustrative Embodiment

A six-cylinder diesel engine installed in a Ford 7000 cargo truck was used as a proof of concept test project. The engine was originally made in Brazil, and had been used commercially for approximately 160,000 miles before being procured for the present testing. The characteristics of the engine are listed in Table 1 below.

20   The 6.6L engine includes 6 cylinders in an in-line configuration. The engine utilizes a cast iron block and head. The engine does not utilize liners in the bores. The head contains 6 intake and 6 exhaust valves, one of each per cylinder.

Table 1

No of Cylinders:	6
Engine Displacement:	6.6 L
Engine Bore:	111.8 mm
Engine Stroke:	111.8 mm
Piston Diameter:	111.34 mm
Intake Valve Diameter:	47.99 mm
Exhaust Valve Diameter:	42.74 mm
Compression Ratio:	17.5:1
Surface Area of Piston (SA_p) (based on Piston Diameter):	9736 mm
Surface Area of Combustion Chamber:	6573 (Estimate)
Surface Area of Valves:	3243.4
Coated Surface Area (SAC):	9816
Ratio SAC to SA_p:	1.008

An initial emissions test in accordance with the New Jersey Methodology yielded an opacity rating of 25.6. The engine was cleaned using MotorVac™ equipment. The

5   MotorVac™ equipment uses a diesel fuel fortified with cleaning agents to remove deposits from the fuel systems and combustion chamber of the diesel engine. An engine being cleaned using the MotorVac™ is operated with the substitute fuel to cause the fortified diesel fuel to be circulated through the engine.

Following completion of the cleaning process, the engine was emissions tested

10   utilizing the original uncoated cast iron head. In accordance with the New Jersey opacity test, the engine yielded an opacity rating of 19.8. The cast iron head was then coated in accordance with the present process with a 4-5 mil thick coating of no more than 0.07% carbon, between 15 and 17% chromium, 4% nickel, 2.75% copper, and 75% iron and trace elements (this composition is commonly called "17-4 Stainless Steel"). The engine was

15   then again tested in accordance with the New Jersey opacity testing standard, and yielded an opacity rating of 17.6.

As a means of correlating the amount of coated area within the combustion chamber to the total combustion chamber surface area, the coated area of a single combustion chamber may be expressed as a ratio of the coated area to the area of the combustion face of the piston, hereafter called the coating factor. Using such a measurement allows the ratio to

5   be expressed without requiring definition of a fixed combustion chamber area, since the combustion ratio surface varies as the piston reciprocates.

For the engine of the present illustration, the diameter of the bore is 111.8 mm. Due to the necessity of under sizing the piston relative to the bore, the piston has a minimum allowable diameter of 111.34 mm. Accordingly, the area of the combustion face is

10   approximately 9736 mm^2 (assuming a flat top piston). If the combustion face of a 47.99 mm intake valve were coated, the surface area of the coating would be approximately 1808 mm^2, yielding a coating factor of approximately .185. If both the combustion face 126 of the piston 102 and the face 124 of the intake valve 120 were coated, the coating factor would be approximately 1.185. It is evident from this that the coating factor can exceed unity, since

15   the total area bounding the combustion includes the area of the combustion face as well as the area of the pocket 118, valve faces 120, 128, and exposed portions of the bore 102.

In the sample engine embodiment, the interior surface of the combustion chamber and the faces of the valves were coated. The combustion face of the piston, and the walls of the bore remained uncoated. It is estimated that the surface area of the coated portion of the

20   combustion chamber was approximately 9816 mm^2, yielding a coating factor of approximately 1.008. As noted above, this engine was run in both uncoated and coated conditions. The operating efficiency of the engine as indicated by emissions from the engine were as shown in Table 2.

-17-

Table 2

Configuration	Description	Opacity
Baseline		26.8
After MotorVac		19.8
Coated (after MotorVac)		17.6

The application of the coating was not limited to the interior surface of the combustion chamber, but rather extended onto the mating surface of the head where the

5   head mates to the engine block. It is important to note that the mating surface of the head was milled prior to coating to remove an equivalent thickness to the coating thickness to mitigate any effects that could have been caused by increased combustion volume resultant from the additional thickness of the coating on the mating surface.

Second Illustrative Embodiment

10   The coating of the present invention has also been applied to a single cylinder Yanmor TS180C research engine. The research engine uses a typical cross flow head, as shown in Figure 4. The engine also utilizes direct injection. The parameters of the engine were as follows:

Table 3

Engine Displacement:	8661 L
Engine Bore:	102mm
Engine Stroke:	106mm
Piston Diameter:	101 mm (estimate)
Intake Valve Diameter:	42.7 mm
Exhaust Valve Diameter:	33.5 mm
Compression Ratio:	19.8
Surface Area of Piston (SAp) (based on est. Piston Diameter):	8011.6 mm^2
Surface Area of Combustion Chamber:	5890 mm^2 (est.)
Surface Area of Valves:	2313.4 mm^2
Coated Surface Area (SAC):	8200 mm^2 (est.)
Ratio SAC to SAp:	1.023

The performance improvements resultant from coating the head and valves (which

5   yielded a 1.023 SAC to SA_p ratio) were as shown in the following table. The mode 4 data

appears to yield aberrant data, however this is believed due to effects associated with the

slow speed in conjunction with the single cylinder configuration. As averaged between the

various modes, the resultant improvements were as follows:

10   **Table 4**

Constituent	Baseline	Coated Head	% Change
HC	1.101877 g/kW-hr	.855357 g/kW-hr	-22.4%
CO	3.66792 g/kW-hr	3.66792 g/kW-hr	-22.1%
CO_2	908.0019g/kW-hr	983.3241 g/kW-hr	+8.3%
NO	5.867477 g/kW-hr	8.17224 g/kW-hr	+39.3%
NO_2	0.853066 g/kW-hr	.543094 g/kW-hr	-36.3%
Particulate (PM)	1.937068 g/kW-hr	1.392242 g/kW-hr	-28.1%

Baseline
Mode IV

mair/mfuel 14.673652

MAF (freq)	3143	Hz	Air Fuel Ratio	95.1		HC	0.0373	g/min	Brake Power	1.50	kW
Mass Air Flow	803	g/min	Exhaust Density	0.843	kg/m3	CO	0.180	g/min	HC	1.49	g/kW-hr
Fuel Consumption	8.44	g/min	Mass Exhaust	811	g/min	CO_2	26.9	g/min	CO	7.22	g/kW-hr
Exhaust Temp.	154	°C	Volume Exhaust	0.962	m3/min	NO	0.216	g/min	CO_2	1076	g/kW-hr
HC	92.5	ppm	Moles in Exhaust	27.5	mol/min	NO_2	0.0372	g/min	NO	8.65	g/kW-hr
CO	235	ppm	HC	0.00254	mol/min	HC	4.41	g/kg fuel	NO_2	1.49	g/kW-hr
CO_2	31375	ppm	CO	0.00644	mol/min	CO	21.4	g/kg fuel	Fuel Consumption	338	g/kW-hr
NO	262	ppm	CO_2	0.611	mol/min	CO_2	3184	g/kg fuel	Particulate	5.04	g/kg fuel
NO_2	29.5	ppm	NO	0.00720	mol/min	NO	25.6	g/kg fuel	Particulate	1.70	g/kW-hr
speed	1380	rpm	NO_2	0.000809	mol/min	NO_2	4.41	g/kg fuel			
load	7.65	ft-lb	Theoretical CO_2	22243 ⟶	% Difference	41.1					
particulate mass	2.86	mg									

Mode III

MAF (freq)	3479	Hz	Air Fuel Ratio	59.3		HC	0.0995	g/min	Brake Power	3.83	kW
Mass Air Flow	1095	g/min	Exhaust Density	0.704	kg/m3	CO	0.214	g/min	HC	1.56	g/kW-hr
Fuel Consumption	18.5	g/min	Mass Exhaust	1114	g/min	CO_2	59.5	g/min	CO	3.34	g/kW-hr
Exhaust Temp.	238	°C	Volume Exhaust	1.58	m3/min	NO	0.387	g/min	CO_2	931	g/kW-hr
HC	180	ppm	Moles in Exhaust	37.7	mol/min	NO_2	0.0671	g/min	NO	6.05	g/kW-hr
CO	202	ppm	HC	0.00679	mol/min	HC	5.39	g/kg fuel	NO_2	1.05	g/kW-hr
CO_2	49690	ppm	CO	0.00763	mol/min	CO	11.6	g/kg fuel	Fuel Consumption	289	g/kW-hr
NO	342	ppm	CO_2	1.35	mol/min	CO_2	3225	g/kg fuel	Particulate	9.88	g/kg fuel
NO_2	38.7	ppm	NO	0.0129	mol/min	NO	20.9	g/kg fuel	Particulate	2.85	g/kW-hr
speed	1773	rpm	NO_2	0.00146	mol/min	NO_2	3.63	g/kg fuel			
load	15.2	ft-lb	Theoretical CO_2	35874 ⟶	% Difference	38.5					
particulate mass	8.93	mg									

13.23

Mode II

MAF (freq)	3703	Hz	Air Fuel Ratio	44.8		HC	0.112	g/min	Brake Power	6.63	kW
Mass Air Flow	1313	g/min	Exhaust Density	0.588	kg/m3	CO	0.311	g/min	HC	1.01	g/kW-hr
Fuel Consumption	29.3	g/min	Mass Exhaust	1342	g/min	CO_2	96	g/min	CO	2.82	g/kW-hr
Exhaust Temp.	340	°C	Volume Exhaust	2.284	m3/min	NO	0.580	g/min	CO_2	865	g/kW-hr
HC	167	ppm	Moles in Exhaust	45.4	mol/min	NO_2	0.0823	g/min	NO	5.25	g/kW-hr
CO	245	ppm	HC	0.00760	mol/min	HC	3.80	g/kg fuel	NO_2	0.745	g/kW-hr
CO_2	68148	ppm	CO	0.0111	mol/min	CO	10.6	g/kg fuel	Fuel Consumption	265	g/kW-hr
NO	426	ppm	CO_2	2.17	mol/min	CO_2	3260	g/kg fuel	Particulate	7.13	g/kg fuel
NO_2	39.4	ppm	NO	0.0193	mol/min	NO	19.8	g/kg fuel	Particulate	1.89	g/kW-hr
speed	2007	rpm	NO_2	0.00179	mol/min	NO_2	2.81	g/kg fuel			
load	23.3	ft-lb	Theoretical CO_2	47824 ⟶	% Difference	42.5					
particulate mass	8.50	mg									

Mode I

MAF (freq)	3811	Hz	Air Fuel Ratio	35.8		HC	0.105	g/min	Brake Power	9.01	kW
Mass Air Flow	1424	g/min	Exhaust Density	0.495	kg/m3	CO	0.506	g/min	HC	0.700	g/kW-hr
Fuel Consumption	39.7	g/min	Mass Exhaust	1463	g/min	CO_2	131	g/min	CO	3.37	g/kW-hr
Exhaust Temp.	454	°C	Volume Exhaust	2.96	m3/min	NO	0.779	g/min	CO_2	871	g/kW-hr
HC	145	ppm	Moles in Exhaust	49.5	mol/min	NO_2	0.0750	g/min	NO	5.19	g/kW-hr
CO	365	ppm	HC	0.00717	mol/min	HC	2.65	g/kg fuel	NO_2	0.499	g/kW-hr
CO_2	87506	ppm	CO	0.0181	mol/min	CO	12.8	g/kg fuel	Fuel Consumption	264	g/kW-hr
NO	524	ppm	CO_2	2.98	mol/min	CO_2	3296	g/kg fuel	Particulate	5.82	g/kg fuel
NO_2	32.9	ppm	NO	0.0260	mol/min	NO	19.6	g/kg fuel	Particulate	1.54	g/kW-hr
speed	2199	rpm	NO_2	0.00163	mol/min	NO_2	1.89	g/kg fuel			
load	28.9	ft-lb	Theoretical CO_2	60060 ⟶	% Difference	45.7					
particulate mass	8.61	mg									

ISO 8178 Weighted Average Totals

HC	1.101877 g/kWh
CO	3.66792 g/kWh
CO_2	908.0019 g/kWh
NO	5.867477 g/kWh
NO_2	0.853066 g/kWh
Particulate	1.937068 g/kWh

TABLE 5

Coated Head

Mode IV

Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit
MAF (freq)	3191	Hz	Air Fuel Ratio	89.4		HC	0.0448	g/min	Brake Power	1.45	kW
Mass Air Flow	842	g/min	Exhaust Density	0.817	kg/m3	CO	0.146	g/min	HC	1.85	g/kW-hr
Fuel Consumption	9.41	g/min	Mass Exhaust	851	g/min	CO_2	30.0	g/min	CO	6.05	g/kW-hr
Exhaust Temp.	168	°C	Volume Exhaust	1.04	m3/min	NO	0.338	g/min	CO_2	1240	g/kW-hr
HC	106	ppm	Moles in Exhaust	28.8	mol/min	NO_2	0.0264	g/min	NO	14.0	g/kW-hr
CO	181	ppm	HC	0.00305	mol/min	HC	4.76	g/kg fuel	NO_2	1.09	g/kW-hr
CO_2	49438	ppm	CO	0.00523	mol/min	CO	15.5	g/kg fuel	Fuel Consumption	389	g/kW-hr
NO	391	ppm	CO_2	0.68	mol/min	CO_2	3189	g/kg fuel	Particulate	7.97	g/kg fuel
NO_2	19.9	ppm	NO	0.0113	mol/min	NO	35.9	g/kg fuel	Particulate	3.10	g/kW-hr
speed	1393	rpm	NO_2	0.000574	mol/min	NO_2	2.80	g/kg fuel			
load	7.34	ft-lb	Theoretical CO_2	23672 → % Difference	109						
particulate mass	4.81	mg									

Mode III

Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit
MAF (freq)	3522	Hz	Air Fuel Ratio	57.5		HC	0.0815	g/min	Brake Power	3.79	kW
Mass Air Flow	1136	g/min	Exhaust Density	0.678	kg/m3	CO	0.222	g/min	HC	1.29	g/kW-hr
Fuel Consumption	19.7	g/min	Mass Exhaust	1156	g/min	CO_2	64	g/min	CO	3.51	g/kW-hr
Exhaust Temp.	258	°C	Volume Exhaust	1.70	m3/min	NO	0.521	g/min	CO_2	1008	g/kW-hr
HC	142	ppm	Moles in Exhaust	39.1	mol/min	NO_2	0.0555	g/min	NO	8.24	g/kW-hr
CO	202	ppm	HC	0.00555	mol/min	HC	4.13	g/kg fuel	NO_2	0.88	g/kW-hr
CO_2	79181	ppm	CO	0.00792	mol/min	CO	11.2	g/kg fuel	Fuel Consumption	312	g/kW-hr
NO	444	ppm	CO_2	1.45	mol/min	CO_2	3228	g/kg fuel	Particulate	6.53	g/kg fuel
NO_2	30.9	ppm	NO	0.0174	mol/min	NO	26.4	g/kg fuel	Particulate	2.04	g/kW-hr
speed	1761	rpm	NO_2	0.00121	mol/min	NO_2	2.81	g/kg fuel			
load	15.2	ft-lb	Theoretical CO_2	37022 → % Difference	113.9						
particulate mass	6.08	mg									

Mode II

Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit
MAF (freq)	3703	Hz	Air Fuel Ratio	43.9		HC	0.0618	g/min	Brake Power	6.42	kW
Mass Air Flow	1313	g/min	Exhaust Density	0.568	kg/m3	CO	0.221	g/min	HC	0.578	g/kW-hr
Fuel Consumption	29.9	g/min	Mass Exhaust	1343	g/min	CO_2	98	g/min	CO	2.06	g/kW-hr
Exhaust Temp.	361	°C	Volume Exhaust	2.366	m3/min	NO	0.768	g/min	CO_2	913	g/kW-hr
HC	92.7	ppm	Moles in Exhaust	45.5	mol/min	NO_2	0.0485	g/min	NO	7.18	g/kW-hr
CO	173	ppm	HC	0.00421	mol/min	HC	2.07	g/kg fuel	NO_2	0.453	g/kW-hr
CO_2	117828	ppm	CO	0.00788	mol/min	CO	7.38	g/kg fuel	Fuel Consumption	280	g/kW-hr
NO	563	ppm	CO_2	2.219	mol/min	CO_2	3263	g/kg fuel	Particulate	2.75	g/kg fuel
NO_2	23.2	ppm	NO	0.02560	mol/min	NO	25.7	g/kg fuel	Particulate	0.770	g/kW-hr
speed	1995	rpm	NO_2	0.001054	mol/min	NO_2	1.62	g/kg fuel			
load	22.7	ft-lb	Theoretical CO_2	48801 → % Difference	141						
particulate mass	3.34	mg									

Mode I

Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit
MAF (freq)	3827	Hz	Air Fuel Ratio	33.9		HC	0.0707	g/min	Brake Power	8.88	kW
Mass Air Flow	1441	g/min	Exhaust Density	0.470	kg/m3	CO	0.291	g/min	HC	0.478	g/kW-hr
Fuel Consumption	42.5	g/min	Mass Exhaust	1483	g/min	CO_2	140	g/min	CO	1.97	g/kW-hr
Exhaust Temp.	494	°C	Volume Exhaust	3.16	m3/min	NO	0.927	g/min	CO_2	949	g/kW-hr
HC	96.0	ppm	Moles in Exhaust	50.2	mol/min	NO_2	0.0156	g/min	NO	6.26	g/kW-hr
CO	207	ppm	HC	0.00482	mol/min	HC	1.66	g/kg fuel	NO_2	0.11	g/kW-hr
CO_2	167474	ppm	CO	0.01041	mol/min	CO	6.86	g/kg fuel	Fuel Consumption	287	g/kW-hr
NO	615	ppm	CO_2	3.19	mol/min	CO_2	3307	g/kg fuel	Particulate	4.12	g/kg fuel
NO_2	6.8	ppm	NO	0.0309	mol/min	NO	21.8	g/kg fuel	Particulate	1.18	g/kW-hr
speed	2197	rpm	NO_2	0.000339	mol/min	NO_2	0.37	g/kg fuel			
load	28.5	ft-lb	Theoretical CO_2	63592 → % Difference	163						
particulate mass	6.44	mg									

ISO 8178 Weighted Average Totals

	Value	Unit
HC	0.855357	g/kWh
CO	2.858434	g/kWh
CO_2	983.3241	g/kWh
NO	8.17224	g/kWh
NO_2	0.543094	g/kWh
Particulate	1.392242	g/kWh

	Coated	Baseline	% Reduction
HC	0.855357	1.101877	22.4%
CO	2.858434	3.66792	22.1%
CO_2	983.3241	908.0019	-8.3%
NO	8.17224	5.867477	-39.3%
NO_2	0.543094	0.853066	36.3%
Particulate	1.392242	1.937068	28.1%

TABLE 6

The raw data associated with the various runs used to arrive at the above reductions is provided in Tables 5 and 6. Table 5 represents data associated with the baseline engine. Table 6 represents data associated with the use of the coated cylinder head. Four test sets were conducted for both baseline and coated conditions, with the engine rpm being set in

5   accordance with ISO 8174 Part 4.

The above data illustrate the potential for reduction of particulate matter (hereafter "PM") constituents in the exhaust stream. Also, unburned hydrocarbons and carbon monoxide emissions are reduced. The amount of the carbon dioxide constituent showed an increase, indicative of a more complete combustion of the hydrocarbon based fuel.

10   Using the characteristics of the Yanmar engine, as shown in Figure 3, allows examination of the effect of coating various surfaces on the SAC to SA_p ratio. The engine has a estimated piston surface area of 8011.6 mm^2. The piston (not shown) has an estimated diameter of 101 mm, as compared to the bore diameter of 102 mm. The pocket 302 formed in the head 304 is fairly flat, with the area surrounding the direct injection port 306 being

15   pocketed. The surface area of the pocket is approximately 5890 mm^2. The surface area of a top ring (not shown) would be approximately 91 mm^2. If the rings were the only coated component, the SAC to SAp ration would be approximately 1.135. By coating only the top surface of the piston, an SAC to SAp ratio of 1 can be achieved. Coating the top surface of the piston and the pocket of the head (but not the valve faces) would yield an SAC to SAp

20   ratio of approximately 1.73. Coating the pocket 302 of the head 304 and the intake valve face 308 and the exhaust valve face 310 would yield an approximate SAC to SAp ratio of 1.023.

Application Process

The coatings of the present invention may be applied to the combustion surfaces using a high-velocity-oxygen-flame process. Other suitable known application processes may also be used. It is believed that utilization of direct current (DC) heating of an engine

5   component being coated promotes the bonding between the component and the coating. It is also believed that the use of the DC current generates an associated induced magnetic effect, further promoting the bonding between the coating and a component being coated. Alternately, the coating may be applied

using a plasma process. The plasma process may not, however, create the same strength of bond between the coating and the component.

Reconditioned Head Market

5   One significant advantage of the present coating technology is the ability of the coating to be a component involved in the engine reconditioning process. Material frequently is removed from combustion chamber surfaces during operation or restoration. Particularly, machining may be required in order to correct surface tolerances where material removal has been such that components can no longer meet specifications.

10   Previously, the components would be discarded since tolerances could not be met. Application of the present coating allows material to be added, potentially allowing previously un-useable components to be returned to service. The addition of the material may cover surfaces which are typically machined during a rebuilding process. The coating of the present invention does not necessarily prevent such machining. Accordingly, valve

15   seats and the mounting surface between the head 304 and the block (not shown) may be accomplished using standard methods.

Additional Effects

As is apparent from the test data, one artifact of the use of the present coating is an increased exhaust temperature. This effect is believed to be associated with the additional

20   chemical reduction of hydrocarbon molecules. The temperature of the exhaust stream may affect the performance of downstream catalysts. The elevated temperatures associated with the present invention may allow the downstream catalytic material to have a greater chemical effect, as well as assist the catalytic material in regenerating. Accordingly, the

efficiency of down-stream catalysts may be improved due to the higher exhaust

temperatures associated with the present coating.

The energy of the exhaust stream has been used to drive turbochargers, which use the

exhaust stream energy to drive a compressor that compresses the fuel-air charge before it

5   enters the combustion chamber. The efficiency of a turbocharger is dependant on the

different between the upstream and downstream pressures and temperatures. Higher

efficiency in the conversion of energy contained within the exhaust stream into mechanical

energy therefore may accrue in conjunction with the use of the present coatings, as the

higher exhaust stream temperature may result in higher gas volume for a given air-fuel

10   charge.

Application to Internal Combustion Engines Using Fuels other than Diesel Fuel

Although the presently preferred embodiment of the invention envisions application

of the coating of the present invention to combustion surfaces of a diesel fueled engine, the

coating may be applied to other engines using fuels which rely on the oxidation of

15   hydrocarbon molecules as an energy source. Such fuels may include petroleum based fuels,

alcohol based fuels, gaseous fuels such as natural gas or propane, or fuels synthesized from

other sources. The catalytic effect of the nickel surface on hydrocarbon fuels using lighter

fractions may be less pronounced than with the diesel fuels, however the benefit of

application of the coating of the present invention may be warranted as lower emission

20   requirements and higher fuel prices affect the operational constraints of internal combustion

engines.

One particular application to which the present invention is believed amenable are

engines using dimethyl ether (CH_3OCH_3), either in straight diesel cycle, spark assisted

ignition, or spark ignited engines. Dimethyl ether is believed to be an alternate fuel for commercial diesel engines. The use of dimethyl ether in diesel cycle engines has yielded reduced NOx emissions, however HC and CO emissions are increased. It is believed that the use of a nickel coating applied to the combustion chamber of an internal combustion engine using dimethyl ether would therefore exhibit reduced NOx, CO and HC emissions due to the inherent qualities of the dimethyl ether in conjunction with the catalytic reaction associated with the nickel coating.

The present invention may be embodied in other specific forms than the embodiments described above without departing from the spirit or essential attributes of the invention. Accordingly, reference should be made to the appended claims, rather than the foregoing specification, as indicating the scope of the invention.